Synopsis

Micro/nano-structural characteristics of functional materials play a crucial role in their properties. In that spirit, it is of utmost importance to explore the 'room at the bottom', to characterize the functional nanomaterials to the smallest possible scale. Transmission electron microscopes have the capability to perform imaging, diffraction, and spectroscopy and are thus indispensable for studying functional nanomaterials. Furthermore, in-situ experiments in a TEM give a way to observe processes in-action, imparting a capability of 'see'ing a process.

This thesis work has exploited electron microscopy for investigating various nanomaterials, enabling to obtain a wealth of information and insights leading to their applications. Keeping in mind the simplicity and importance of wet chemical synthesis route, the optimum reaction parameters required for the nucleation and growth of desired nanostructures is explored. In combination with various other characterization techniques, the formation mechanism, structure and stability of synthesized nanostructures and their hybrids are investigated primarily targeting the electronic properties and catalytic applications.

The entire thesis study is organized as follows:

Chapter 1 gives a general introduction of nanomaterials and their role in different fields of application. The need for shape, size and phase control of nanostructures and their hybrids has been described. Classification of these nanomaterials and the importance of tuning their property based on their dimensionality are highlighted. The problems and challenges in stabilization of the materials at nanoscale are discussed elaborating the existing methodologies used to overcome the challenges. The detailed information of the synthetic protocol, basic techniques utilized to characterize the materials in study is reported in the respective chapters.

Chapter 2 describes various methods and techniques used to synthesize and characterize various functional nanostructures synthesized in this thesis via wet-chemical synthesis. A very brief description of the working principles of different techniques used in the characterization of the materials is presented.

Chapter 3 exploits the Kirkendall mechanism at nanoscale for the formation of hollow nanotubes of Zn_2SiO_4 and SiO_2 using a two-step process: a wet-chemical synthesis of core–shell nanostructure of $ZnO@SiO_2$ followed by thermal annealing. While annealing in air leads to the formation of hollow Zn_2SiO_4, annealing under reducing atmosphere leads to the formation of SiO_2 nanotubes. While the imaging reveals the operative Kirkendall process, diffraction characteristics and high-resolution (HR) TEM imaging pinpoints the temperature of nanotube formation. Detailed *in-situ* TEM has been carried out for Zn_2SiO_4 nanotube formation from a $ZnO@SiO_2$ core-shell structure results clearly indicating void nucleation at the interface of ZnO and the silica shell and the evolution of the silicate phase through the Kirkendall effect. Furthermore, the ambience of the reaction was found to render a profound effect on the product, as SiO_2 tubes were forming under a reducing condition. Detailed energy dispersive X-ray spectroscopy (EDS) confirms that the process happens through nanoscale evaporation of ZnO from the core-shell structure. These nanotubes, having a high surface area, exhibit good Uranium adsorption property.

Chapter 4 deals with synthesis, characterization and electrical transport properties of ultrathin Te nanowires. Experiments clearly show that Te nanowires undergo a semiconductor to metal transition on adsorption of NO_2 gas on the nanowire surface. Corresponding DFT simulations show that a new state appears at the Fermi level of the Te nanowires upon exposure to NO_2. Such adsorption-mediated fundamental change in electronic structure can further be exploited to use the Te nanowires as sensors. We illustrate this concept by adsorption of H_2S on Te nanowire, and how that the electronic structure shows an enhanced band gap. This understanding can be exploited in the design of gas-sensors with these nanowires.

The microstructure and phase has been found to be of importance for the electrochromic properties of tungsten oxide. Chapter 5 demonstrates the electrochromic applications of nanoscale WO_3. Tuning synthesis parameters, it has been possible to tune phase-selection of WO_3, leading to orthorhombic and hexagonal phases. Microstructural characterization shows that orthorhombic phase has 2-D plate morphology, while the hexagonal phase has 1-D rod morphology. Using crystallographic arguments and DFT simulations, along with the microstructure, the growth mechanism of these phases has been rationalized in detail. Their electrochromic property has as well been explored in detail through electrochemical measurements and simulations.

An extension of this is incorporation of Mo into WO_3 lattice to tune the electronic properties. Chapter 6 is based on spectroscopic and structural characterization of solid solution of $W_xMo_{1-x}O_3$ system. Experiments show that Mo-incorporation can happen only in a hydrated orthorhombic phase of WO_3, with plate morphology, and has an upper limit of 60% lattice substitution of W, and renders an effect on the band gap of the material.

Continuing in the same spirit of nanoscale characterization, detailed electron microscopy has been carried out for two types of supported catalysts – one, cerium oxide supported Pt nanoparticles used for CO oxidation, and two, reduced graphitic oxide supported PtBi nanoparticles for methanol oxidation.

Chapter 7 details the synthesis of intermetallic PtBi catalyst on graphitic support through an ultrafast microwave assisted route. This rapidly fabricated intermetallic PtBi catalyst shows a mixed phase of PtBi and $PtBi_2$. Their structure, composition, and formation mechanism have been studied in detail through diffraction and spectroscopic methods. The post-catalysis nanoscale spectroscopic analysis shows that the $PtBi_2$ nanoparticles undergo a higher degree of leaching under electrochemical conditions.

Chapter 8 presents a detailed *ex-situ* and *in-situ* transmission electron microscopy (TEM) studies of Pt nanoparticles supported on different facets of ceria. The role of metal-support interface on the stability of the catalyst under various operational reaction conditions are examined presenting an understanding of the coarsening mechanism. Statistical analysis of TEM data reveals the pathway followed during sintering of the Pt nanoparticles over different planes of ceria in different atmosphere.

Finally in conclusion, different possibilities and prospects that the study leads to, is highlighted.